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Structure and Rotational Isomerism of Chloroacetyl Chloride Molecules

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Abstract—The structure of chloroacetyl chloroide ($CH_2ClCOCl$) molecule in different conformations arising from rotation of the CH_2Cl group about the C–C bond was determined by the Hartree–Fock RHF/6-31G(d) quantum-chemical calculations. The energy difference between the two stable rotamers was estimated at 5.9 kJ mol^{-1}, and barriers to intramolecular reorientations of the CH_2Cl group were calculated.

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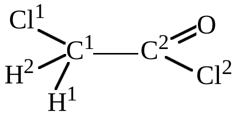
We previously [1] studied the structure and internal rotation of trichloroacetyl chloride molecule ($CCl_3 \cdot COCl$) by nonempirical quantum-chemical calculations. Reorientation of the trichloromethyl group about the C–C bond was found to be described in terms of a threefold equal-well potential. The goal of the present study was to elucidate the shape of potential curve for the rotational motion of the partly chlorinated methyl group in chloroacetyl chloride ($CH_2ClCOCl$, **I**) and determined the corresponding structural and energetic parameters of its molecule.

According to the experimental data obtained by the gas-phase electron diffraction method [2], chloroacetyl chloride exists as two rotational isomers, *cis* and *gauche*, the first of these being more stable. The same conclusion was drawn previously [3–7] from the data of optical and microwave spectroscopy.

In order to determine the geometric parameters of molecule **I** in equilibrium and transition states arising from rotation of the CH_2Cl group about the C–C bond and the potential barriers separating these states, we performed nonempirical quantum-chemical calculations of the chloroacetyl chloride molecule on the Hartree–Fock level (RHF) using the 6-31G(d) basis set. The calculations were performed with the aid of Gaussian-94W software [8]. The atoms in molecule **I** were numbered as follows:



The results showed that the most stable conformer of **I** is characterized by eclipsed orientation of the $C^1–Cl^1$ and $C^2=O$ bonds, the dihedral angle $Cl^1C^1C^2O$ (φ) being equal to zero. This *cis* structure is characterized by a symmetry plane which includes the $C^1–Cl^1$, $C^1–C^2$, $C^2=O$, and $C^2–Cl^2$ bonds (see table). The corresponding geometric parameters are given in the table together with those obtained experimentally by gas-phase electron diffraction [2] and calculated by molecular mechanics [9]. On the whole, the data obtained by different methods do not contradict each other, but an underestimated C=O bond length determined by the RHF/6-31G(d) calculations should be noted (this is consistent with the known [1, 10–13] tendency of that procedure as applied to carbonyl group).

The structure and energy parameters of rotational isomers of **I** were calculated by varying the angle φ from 0° (major *cis* conformer) to 360° through a step of 15° with optimization of all other geometric parameters at each fixed value of φ. As a result, we obtained potential function $\Delta E(\varphi)$ for internal rotation, where ΔE is the relative energy of the molecule, i.e., the difference between the total energy at a given value of φ and its minimal value (at $\varphi = 0°$, see figure). Insofar as the potential curve in the φ range from 0° to 360° is symmetric relative to the vertical line passing through the point $\varphi = 180°$, the energy parameters are given in the figure only for the φ range from 0° to 180° inclusively.

It is seen that rotation of the CH_2Cl group in molecule **I** is described by orientational potential with unequal wells and a global minimum at $\varphi = 0°$, which corresponds to the most stable *cis* conformer. The local minimum at $\varphi = 113°$ is occupied by the less stable *gauche* conformer. The energy difference

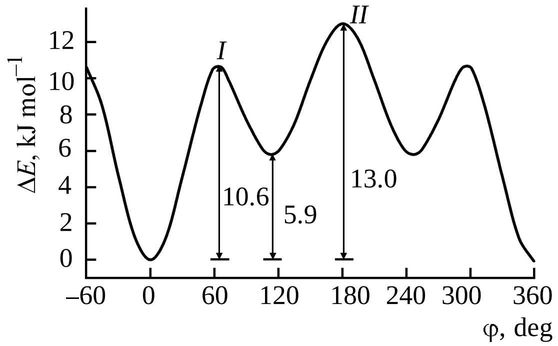
Bonds lengths (d, Å), bond angles (ω, deg), torsion angles (τ, deg), and total energies (E) of chloroacetyl chloride (**I**) in equilibrium (*cis* and *gauche* conformers) and transition states, calculated by the RHF/6-31G(d) method, determined experimentally by gas-phase electron diffraction [2], and calculated by molecular mechanics [9]

Parameter	RHF				Gas-phase electron diffraction[a]	Molecular mechanics	
	cis	transition state *I*	*gauche*	transition state *II*		*cis*	*gauche*
			Bond				
$C^1–C^2$	1.513	1.520	1.516	1.524	1.521	1.508	1.508
$C^1–Cl^1$	1.765	1.777	1.777	1.765	1.782	1.780	1.780
$C^1–H^1$	1.079	1.075	1.078	1.079	1.062	1.096	1.096
$C^1–H^2$	1.079	1.079	1.077	1.079	1.062	1.096	1.096
$C^2–O$	1.163	1.166	1.168	1.170	1.182	1.186	1.186
$C^2–Cl^2$	1.775	1.766	1.761	1.749	1.772	1.799	1.799
			ω angle				
$Cl^1C^1C^2$	112.5	110.3	111.6	118.2	112.9	112.2	112.2
$H^1C^1C^2$	108.9	112.1	110.4	106.5		110.3	109.5
$H^2C^1C^2$	108.9	107.7	107.6	106.5		110.4	110.4
$Cl^1C^1H^1$	109.0	108.3	108.0	108.5		107.5	107.5
$Cl^1C^1H^2$	109.0	107.9	108.4	108.5		107.5	108.2
$H^1C^1H^2$	108.6	110.5	110.9	108.4	109.5	109.2	108.6
C^1C^2O	128.4	124.8	124.2	119.7	126.9	126.6	127.2
$C^1C^2Cl^2$	110.3	114.0	114.5	119.2	110.0	113.1	112.5
			τ angle				
$Cl^1C^1C^2O$	0.0	64.0	113.0	180.0	0.0 and 116.4	0.0	119.7
$Cl^1C^1C^2Cl^2$	180.0	–117.3	–68.9	0.0			
$H^1C^1C^2O$	120.9	–175.3	–126.9	–57.8			
$H^2C^1C^2O$	–120.9	–53.5	–5.8	57.8			
			Total energy of the molecule $-(E + 1070)$, au				
	0.721454	0.717432	0.719211	0.716518			

[a] The parameters of both conformers, except for the dihedral angle τ, were assumed to be equal.

between these conformers is 5.9 kJ mol^{-1}, and the barrier from the deepest potential well is 10.6 kJ mol^{-1} (transition state *I* at $\varphi = 64°$). The barriers separating the local minimum from the global minimum and the other local minimum (see figure) were estimated at 4.7 and 7.1 kJ mol^{-1}, respectively. Transition state *II* located at $\varphi = 180°$ and corresponding to an appreciably higher barrier between the local minima is characterized by eclipsed orientation of the $C^1–Cl^1$ and $C^2–Cl^2$ bonds, which gives rise to the strongest repulsion between the two chlorine atoms and hence to the maximal total energy (see figure and table). The $Cl^1C^1C^2$ and $Cl^2C^2C^1$ angles in transition state *II* are larger by 6°–9° than the corresponding angles in the main equilibrium state (*cis* conformer).

The potential curve for internal rotation shown in figure has a shape similar to those found previously for molecule **I** by the gas-phase electron diffraction method and molecular mechanics calculations [2, 9]. While comparing the results of the present study with the data of [2, 9], similarity in φ values corresponding to the equilibrium and transition states of molecule **I** upon rotation of the CH_2Cl group about the C–C bond should be noted. The differences in the energies of the *cis* and *gauche* conformers are also small:



Torsion potential of the chloroacetyl chloride molecule vs. the angle $\varphi(Cl^1C^1C^2O)$.

5.9 kJ mol^{-1} (our data) and 5.5 [2] and 4.2 kJ mol^{-1} [9]. A comparable difference in the energies of these conformers (4.0 kJ mol^{-1}) was reported for molecule **I** in [6].

We can conclude that the geometric and energy parameters of rotational isomers of chloroacetyl chloride, calculated in the present work by the RHF/6-31G(d) nonempirical method, are consistent with the data obtained by other methods. On the other hand, the results of our calculations provide a more complete information on rotational isomerism of chloroacetyl chloride due to rotation of the $ClCH_2$ group about the C–C bond.

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